

IX. "On the Electrolysis of Gases." By J. J. THOMSON, M.A.,
F.R.S., Cavendish Professor of Experimental Physics,
Cambridge. Received June 17, 1895.

In the experiments described in this paper I have used the spectro-scope to detect the decomposition of gases by the electric discharge and the movement of the ions in opposite directions along the discharge-tube.

The method consists in sending the electric discharge through a tube so arranged that the spectra close to the positive and negative electrodes can easily be compared; thus the presence or absence of certain ions at these electrodes can be ascertained. This method is capable of much wider application than the one I previously used in my experiments on the "Electrolysis of Steam" ('Proc. Roy. Soc.,' vol. 52, p. 90), the use of which is attended with very great difficulty for any substance other than steam. The earlier method has, however, the advantage of being a quantitative method—the present one is only qualitative.

In my former experiment with steam, when I worked at atmospheric pressure and varied the length of the spark, I found that when the spark-length exceeded a certain length, d_1 , there was an excess of hydrogen at the negative electrode and of oxygen at the positive, equal in amount to the quantities of hydrogen and oxygen liberated from a water voltameter placed in series with the steam-tube. When the sparks were shorter than a certain length, d_2 , the hydrogen appeared at the *positive*, the oxygen at the *negative* electrode, but the quantity of these gases was again equal to the quantities liberated in a water voltameter placed in series with the steam-tube.

When the spark-length was between d_1 and d_2 the effects were irregular, and there seemed to be no connection between the amounts of gases liberated in the steam-tubes and those liberated in the voltameter.

In the following experiments in which the sparks were of constant length and the pressure was altered, corresponding effects were observed. Within certain limits of pressure definite and perfectly regular evidence of the separation of the ions of the gas sparked through was obtained; and the electrode at which a given ion appeared could be reversed by altering the pressure; there was, however, a range of pressures in which the separation of the ions was either not well marked or was irregular in character.

I shall begin by describing a very simple method of showing the separation of the ions produced by the discharge of electricity through a compound gas such as hydrochloric acid gas, which is

applicable when the discharges through the constituent gases of the compound are of distinct and different colours; this is eminently the case with the hydrochloric acid gas, as the discharge through hydrogen in a capillary tube is red, through chlorine green.

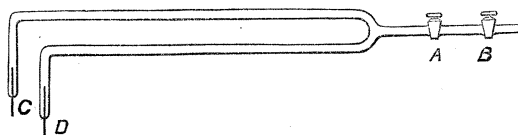
Take a capillary tube of very fine bore, the finer the better (the tube I used was thermometer tubing of the finest bore I could procure), and insert platinum wires for electrodes in two small bulbs blown on the ends of the tube; then fill the tube with HCl gas, allowing it to run through the tube for a considerable time so as to get rid of any extraneous gas, and exhaust the tube so that the gas in it is at a very low pressure. Then when the discharge from a large induction coil passes through the tube, the following phenomena are observed. When first the discharge passes through the tube the colour is uniform throughout and of a greenish-grey; after the discharge has been passing for a little time the end of the tube next the cathode gets distinctly red, whilst that next the anode gets green; this difference in the colour at the ends of the tube goes on increasing until the tube presents a most striking appearance, the part near the cathode being bright red, while that near the anode is a bright green. The difference in colour attains a maximum value, and if the discharge is allowed to run for several hours the contrast between the two ends disappears to a very great extent; the discharge throughout the whole of the tube being pinkish and apparently passing mainly through hydrogen. This is doubtless due to the diffusion through the tube of the hydrogen which in the earlier stages of the discharge had accumulated about the cathode; one advantage of using very narrow tubes is that with them this diffusion is slow. When the tube is in this condition the colour of the discharge sometimes changes suddenly, and for a second or two is green instead of pink, showing that though in the main the discharge passes through hydrogen, it occasionally leaves the hydrogen and passes through the chlorine. This transference of the discharge from one constituent to another of a mixture of gases is not infrequently observed when the gases are mixed in certain proportions.

Some of these capillary tubes showed after the discharge had been passing through them for some time a peculiar patchy appearance, some portions of the tube being a much brighter red than the others, while other portions were green. In some tubes this occurred to such an extent that the discharge showed an irregularly striated appearance. This effect is due, I believe, to gases or moisture condensed on the walls of the capillary tube, and in some cases to irregularities in the chemical composition of the glass. I found that it did not occur if the tube before being used was heated for some time along its whole length to as high a temperature as it would stand without collapsing; this heating would tend to cleanse the walls of the tube. That dif-

ferences in the quality of the gas also conspire to produce these patches is shown, I think, by the following phenomenon. A capillary tube of fine bore containing mercury vapour and a little water vapour developed a well marked red patch; the tube was then heated for some inches in the neighbourhood of the patch. In general heating the tube makes the discharge yellow from the sodium vapour given off from the glass; in this case, however, the whole of the heated portion, with the exception of the patch, turned yellow; the patch itself withstood the heating and continued to show the bright red colour characteristic of hydrogen.

Electrolytic Transport of one Gas through another.—A tube of the shape shown in fig. 1 was made of the finest bore thermometer-tubing; the extremities, C and D, of the tube in which the electrodes

FIG. 1.



were fused were bent down so as to be parallel to each other, and so near together that a slight motion of the tube suffices to bring either of the extremities in front of the slit of the spectroscope. The tube was mounted on a board moved by a lever; by moving this the observer at the spectroscope could readily bring the spectrum of either the positive or negative electrode into the field of view. A side tube, AB, was fused to the middle of the main tube and was provided with two taps; in the space between these taps a small quantity of any gas which it was desired to introduce into the main tube could be imprisoned, and could, by opening the tap A, be introduced into the discharge tube. The experiment consists in filling the main tube with a gas at a low pressure, observing the spectra at the two electrodes, then introducing by the side tube a very small quantity of gas into the main tube, and again observing the spectra at the two electrodes.

A tube was filled with hydrogen and showed no trace of the chlorine spectra; a very small quantity of chlorine was then let in through the side tube (in performing this experiment it is necessary to be careful that only a very small quantity of chlorine is introduced). After the discharge had been running through the tube for a short time, the chlorine spectrum was found to be bright at the positive electrode, though no trace of it could be detected at the negative. When the discharge was kept on for some time, the chlorine spectrum, though still visible at the positive electrode, got fainter; it did not appear at all at the negative. If a considerable

quantity of chlorine was introduced through the side tube, the chlorine spectrum was visible at both electrodes, though it was brighter at the positive than at the negative.

When the induction coil was reversed, so that what was before the positive electrode became the negative, the first effect observed was that the chlorine spectrum flashed out with great brilliancy at the old positive electrode, and was much brighter than at any previous period. This, however, only lasted for a second or two; the chlorine spectrum rapidly faded away and for a time was not visible at either electrode. Soon, however, the chlorine spectrum appeared at the new positive electrode, having thus been transferred from one end of the tube to the other.

On again reversing the coil the same phenomenon was repeated. There was apparently no limit to the number of times this effect may be obtained; at any rate, I have driven the chlorine from one end of a tube to the other 14 times in succession by reversing the coil. The chlorine is always driven to the positive electrode, showing that the chlorine ion carries a charge of negative electricity. The same effect was obtained when a little vapour of bromine was introduced into the tube instead of chlorine. When, however, the capillary tube was filled with chlorine instead of hydrogen, and a little vapour of bromine let into the tube, the bromine went to the *negative electrode* instead of to the positive, as it did when introduced into the hydrogen tube. These experiments suggest that the two gases in the tube combine, and that the compound gas so formed is split up into ions which travel along the tube; that bromine when in combination with hydrogen is the negative ion, and therefore travels to the positive electrode; when, however, it is in combination with chlorine the bromine is the positive ion and travels to the negative electrode.

Another experiment tried was to let a little vapour of sodium into the middle of a capillary tube filled with air at a low pressure. To prevent the sodium vapour condensing on the walls of the tube, the whole tube was placed on a sand-bath and the temperature raised so high that no condensation took place. After the discharge had run through the tube for about two hours the sand was removed from the tube, and the movement of the sodium vapour to the *negative electrode* was very apparent even without using a spectroscope, as there was a great patch of yellow light near the negative electrode and none in any other part of the tube.

Another experiment was to introduce a small quantity of hydrogen into a tube filled with air at a low pressure: the hydrogen made its way to the *negative electrode*. This experiment is a somewhat troublesome one, as it is exceedingly difficult to get these very fine capillary tubes so dry that the spectrum of the discharge does not show the hydrogen lines even before the hydrogen is introduced into the middle

of the tube; indeed I never succeeded in getting rid of the hydrogen lines at the very lowest pressures. By heating the tube and allowing dry air to run through it for a long time, however, I got the tube so dry that it did not show the hydrogen lines at a pressure quite low enough to allow the discharge to pass freely through it. When the tube was in this state and hydrogen was let into the middle of the tube, the hydrogen spectrum appeared at the negative electrode, but not at the positive.

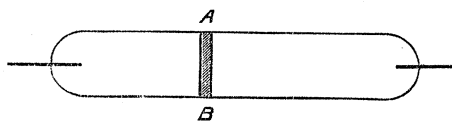
The appearance of hydrogen at the negative electrode when mixed in a discharge tube with other gases has been described by Mr. Baly in a very interesting paper in the 'Philosophical Magazine,' vol. 35, p. 200.

The preceding experiments suggest, I think, that this separation of two gases, A and B, by the discharge is due to the decomposition by the discharge of a chemical compound formed of A and B, in which the A atoms have a charge of electricity of one sign, the B atoms a charge of electricity of the opposite sign; these charged atoms under the influence of the electromotive force in the tube travel in opposite directions. Further, it follows from the experiment with the bromine vapour in an atmosphere of chlorine that the sign of the electrical charge on an atom of the same substance is not invariable, but depends on the substance with which this atom is in combination. We shall find numerous other instances of this change in the sign of the charge on an atom in experiments described in a later part of this paper.

Polarisation of the Electrodes.—This in the electrolysis of liquids is due to the accumulation at the electrodes of ions which have ceased to act as carriers of electricity. We have, I think, distinct evidence of a similar accumulation in the electrolysis of gases. For, as has been already described, after the discharge has been running for some time in one direction, giving the spectrum of some gas at one of the terminals, the spectrum of the gas at that terminal is momentarily brightened to a very great extent by suddenly reversing the direction of the discharge. After the current has been flowing for some time in one direction through, say, Cl in an atmosphere of H, the spectrum of the chlorine, though still visible at the positive electrode, gets faint, the chlorine apparently to a great extent ceasing to carry the discharge; when, however, the current is reversed, the atoms of chlorine can move freely, as they are not obstructed by the electrode, so that immediately after the reversal of the current there is probably more of the discharge carried by the chlorine than at any other time, and the chlorine spectrum is consequently brightest.

Discharge through a Compound Gas.—The separation of the ions by the discharge can be readily observed in a tube of the kind shown in fig. 2.

FIG. 2.



It differs from an ordinary discharge tube merely in having a flat metal plate, AB, fastened across the tube. When the discharge passes through the tube, one side of the plate acts as a positive, the other as a negative, electrode. The tube is mounted on a stand, which the observer at the spectroscope can move by means of a lever so as to bring one side or other of the plate opposite the slit of the spectroscope; a very slight movement of the lever is sufficient to do this, so that the spectra at the two sides of the plate can readily be compared. I found that the results were more satisfactory when the current was kept flowing through the tube in one direction and the tube moved so as to bring the spectra at the two electrodes into the field of view, than when the tube was kept fixed in one position and the current reversed. The latter method, however, suffices to show the separation of the ions in many cases, and it has the advantage of not requiring a plate across the tube; all that is necessary is to use for one of the terminals a disc whose plane is parallel to the slit of the spectroscope.

If the plate AB is thin, it is necessary to fuse it into the glass tube all the way round, otherwise when the pressure is low, the discharge, instead of crossing the plate, goes through any little crevices there may be between the plate and the tube. The easiest way of making the tube is to use a plate about 0.5 cm. thick, cut from an aluminium cylinder which tightly fits the tube; with a plate of this thickness the narrow spaces between the tube and the plate are so long that the discharge goes through the plate rather than through the crevices.

The tube was filled with the gas to be observed and the spectra at the two sides of the plate compared. These spectra were in many cases found to differ in a very remarkable way; it was, however, only in exceptional cases that a line which was bright at one side of the plate was absolutely invisible on the other. The method used was to take two sets of lines, say A and B, as close together in the spectrum as possible, and compare the brightness of these sets of lines on the two sides of the plate; if it was found that the A lines were brighter on the positive side of the plate than on the negative, while on the other hand the B lines were brighter on the negative side of the plate than on the positive, then it was inferred that electrolytic separation had occurred, and that the substance giving the A lines was in excess on the positive side of the plate, that giving the B lines on the nega-

tive. It is not safe to draw any conclusions from the variations in intensity of one line or one group of lines on the two sides of the plate, as the total quantity of light coming from the neighbourhood of the cathode often differs considerably from that coming from the anode. When, however, we get an increase in the brilliancy of one set of lines accompanied by a diminution in the brightness of another set, when we move across the plate we eliminate this source of error. The differences in the spectra at the two sides of the plate are most easily observed at pressures where there is not any very great difference between the luminosity of the cathode and the anode. As was mentioned at the beginning of the paper, there is a range of pressure within which the effects are irregular, and no decided differences are observed between the spectra at the two sides of the plate. It is desirable in these experiments to keep the tube on to the pump as long as the experiment lasts, for the discharge always decomposes the compound gas, and unless the products of decomposition are continually pumped off and replaced by fresh supplies of the compound gas, the spectra of the discharge keep changing. With organic compounds this is especially necessary, as the character of the spectrum often changes entirely very shortly after the commencement of the discharge unless fresh gas is continually introduced.

In the following experiments the current was produced by a large induction coil with a mercury slow break.

When the tube was filled with hydrochloric acid gas at a low pressure, the separation of the hydrogen and chlorine was seen very distinctly, the hydrogen line being much brighter on the side of the plate which acted as the cathode (which we shall call the negative side of the plate) than on the positive side, while the chlorine, on the other hand, was brighter on the positive than on the negative side of the plate.

When the tube was filled with ammonia gas, the hydrogen lines were bright on the negative side of the plate but were absent from the positive side, while on the positive side of the plate there was the positive pole spectrum of nitrogen, and on the negative side of the plate the negative pole spectrum of nitrogen and the hydrogen spectrum.

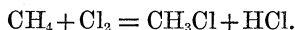
Sulphur Monochloride.—When the tube was filled with the vapour of this substance at a low pressure, the chlorine lines were brighter on the *negative* side of the plate than at the positive, while the sulphur lines were brighter at the positive side than at the negative. Thus the chlorine in this substance behaves in the opposite way to the chlorine in HCl ; in the latter compound the chlorine ion has a charge of negative electricity, while in the sulphur monochloride it has a charge of positive electricity.

Influence of the Chemical Constitution of a Compound on the Sign of the Charge of Electricity on one of its Constituent Atoms.—In many organic compounds an atom of the electro-positive element hydrogen can be replaced by an atom of the electro-negative element chlorine without altering the type of the compound. Thus, for example, we can replace the four hydrogen atoms in CH_4 by chlorine atoms, getting successively the compound CH_3Cl , CH_2Cl_2 , CHCl_3 , and CCl_4 . It seemed of interest to investigate what was the sign of the change of electricity on the chlorine atom in these compounds. The point is of some historical interest, as the possibility of substituting an electro-negative element in a compound for an electro-positive one was one of the chief objections assigned against the electro-chemical theory of Berzelius.

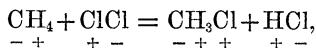
When the vapour of chloroform, CHCl_3 , was placed in the tube, it was found that both the hydrogen and the chlorine lines were bright on the negative side of the plate, while they were absent from the positive side, and that any increase in the brightness of the hydrogen lines was accompanied by an increase in the brightness of those due to chlorine. The spectrum on the positive side of the plate was that called the carbonic oxide spectrum; when first the discharge passed through the tube, the spectrum on the positive side was the so-called candle spectrum, but this very rapidly changed to the carbonic oxide spectrum. The appearance of the hydrogen and chlorine spectra at the same side of the plate was also observed in methylene chloride and in ethylene chloride. Even when all the hydrogen in CH_4 was replaced by chlorine, as in carbon tetrachloride, CCl_4 , the chlorine spectra still clung to the *negative* side of the plate. To test the point still further, I tried the analogous compound silicon tetrachloride, inserting a small jar in the circuit to brighten the spectrum. The chlorine spectrum was again brightest at the *negative* side of the plate, while the silicon spectrum was brightest at the positive. This is a very favourable case for the application of this method, as there are two silicon lines (wave-lengths 5058, 5043) quite close to two chlorine ones (wave-lengths 5102, 5078), so that their relative brightness can easily be compared. The experiment with the silicon tetrachloride is more conclusive than those with the carbon compounds, as with the latter the spectrum on the positive side of the plate is a band spectrum, and since the potential gradient when the discharge is passing is very much steeper on the negative side of the plate than on the positive, the effects observed might be supposed to be due to the circumstances on the negative side being better adapted for the production of line spectra than those on the positive. This explanation is not, however, applicable to the case of silicon tetrachloride, where the spectra on both sides of the plate are line spectra.

From these experiments it would appear that the chlorine atoms in the chlorine derivatives of methane are charged with electricity of the same sign as the hydrogen atoms they displace.

When we can determine the signs of the electrical charges carried by the atoms in a molecule of a compound, we can ascertain whether any given chemical reaction does or does not imply interchange between the electric charges on the atoms taking part in the reaction. Thus take the reaction

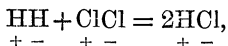


If we represent the sign of the charge of electricity carried by an atom by + or - placed below the symbol representing that atom, we may write the last reaction as



so that this reaction could be produced by a rearrangement of the atoms without any alterations of their electrical charges.

If, however; we take the reaction—



we see that in addition to a rearrangement of the atoms there must in this case be an interchange of electric charges between the atoms; for before combination half the hydrogen atoms had a negative charge, and half the chlorine atoms a positive one, whereas after combination no hydrogen atom has a negative charge, and no chlorine atom a positive one. We may thus distinguish between two classes of chemical reactions, (1) those which do not necessarily require any interchange of the electrical charges carried by the atom, and (2) those which do. It might, perhaps, repay investigation to see whether the occurrence of chemical change is affected by the presence of a third substance in the same way in these classes of chemical combination.

Another point to be considered is the effect of this difference between the chemical actions on the amount of heat developed during chemical combination. When hydrogen and chlorine combine the heat produced may be regarded as the joint effect of three processes:—

1. The splitting up of the molecules ($\begin{smallmatrix} \text{H} & \text{H} \\ + & - \end{smallmatrix}$) and ($\begin{smallmatrix} \text{Cl} & \text{Cl} \\ + & - \end{smallmatrix}$) into the atoms $\begin{smallmatrix} \text{H} & \text{H} & \text{Cl} & \text{Cl} \\ + & - & + & - \end{smallmatrix}$.

2. A transference of electricity by which the negative charge on one atom of hydrogen is replaced by an equal positive charge, while the positive charge on an atom of chlorine is replaced by an equal negative charge.

3. The combination of the positively electrified hydrogen atoms with the negatively electrified chlorine ones to form hydrochloric acid.

In that class of chemical action where the atoms retain their charge (2) is absent, so that if the change in energy occurring in the process (2) were considerable compared with the changes occurring in processes (1) and (3), the thermal effects of the two types of chemical combination ought to differ considerably. If the changes in energy occurring in the process (2) had a great preponderance over those occurring in (1) and (3), the thermal effects produced by the combination of two elements ought to follow very simple laws. For if $2\{H\}$ is the excess of the energy of an atom of hydrogen charged with the negative electron over the energy of the atom charged with the positive electron, $2\{Cl\}$ the excess of the energy of an atom of chlorine charged with the positive electron over the energy of the atom charged with the negative electron, then if we could neglect the energy changes in (1) and (3) compared with those in (2), the mechanical equivalent of the heat developed when a molecule of hydrogen combines with one of chlorine to form two molecules of hydrochloric acid would be equal to $2\{H\} + 2\{Cl\}$. Thus we see that if the energy changes in (2) preponderated largely over those in (1) and (3), the heat produced when an element A combined with another element B to form the compound AB, could be expressed as the sum of two numbers $\{A\}$ and $\{B\}$, where $\{A\}$ depends solely on the element A, $\{B\}$ solely on the element B. In some cases of chemical combination between dilute solutions there seems evidence that the heat produced can be expressed in this way (see Lothar Meyer, "The Evolution of the Doctrine of Affinity," 'Phil. Mag.,' vol. 23, p. 504), but when we attempt to apply the same law to combination between gases, it seems utterly to break down, indicating that in such cases the greater part of the changes in energy occur in the splitting up of one set of molecules and the subsequent formation of others. This view seems to be supported by the phenomena attending the discharge of electricity through rarefied gases, for the smallest difference of potential which can send a discharge through an electrified gas (which we have reason to believe involves the splitting up of molecules into atoms), is very many times the electromotive force required to liberate the ions from an electrolyte, though the latter process requires changes in the electrical charges on the ions. These reasons seem to indicate that we can hardly expect to get any clear indication of the charges carried by the atoms in gaseous compounds from the study of the thermal changes which occur when gases enter into chemical combination.

Vapours of Organic Compounds.—These show very interesting differences between the spectra on the two sides of the plate when

the discharge passes through them. Thus when the discharge first passes through the vapour of ethyl alcohol, C_2H_5O , the spectrum on the positive side of the plate is the candle spectrum, that on the negative side the carbonic oxide spectrum. For some little time after the discharge commenced I could not detect any hydrogen lines on either side of the plate; after a time, however, they appeared on the negative side but not on the positive. If the discharge was kept running for some time without letting a fresh supply of alcohol into the tube, the "candle spectrum" on the positive side of the plate was replaced by the CO spectrum, which now occurred on both sides of the plate, accompanied on the negative side by the hydrogen spectrum. This is the appearance presented by all the compounds of carbon, oxygen, and hydrogen which I examined, when the spark had been passing through them for a considerable time, and it is what would occur if the vapour were decomposed by the spark into carbonic acid, water, and hydrogen.

The appearance of the candle spectrum on the positive side of the plate with the CO on the negative was observed in many other cases. Thus on sparking through a tube filled with CO I could not detect any difference between the spectra on the two sides of the plate, but when a little hydrogen was let into the tube the "candle spectrum" appeared on the positive side of the plate, the carbonic oxide spectrum on the negative. The same effect was observed in a tube filled with cyanogen mixed with a little hydrogen. When the tube was filled with the vapour of methyl alcohol, CH_3OH , the candle spectrum was on the positive side of the plate, the carbonic oxide and hydrogen spectra on the negative; with this vapour, unlike that of ethyl alcohol, I could not detect any stage when the hydrogen spectrum was absent.

The first explanation which occurs to one of this phenomenon is that it is owing to the potential gradient at the negative side of the plate being steeper than that on the positive, so that we may imagine we have a fierce spark on the negative side, a mild one on the positive, and that the fierce spark gives the CO spectrum, the mild one the candle spectrum. There are, however, some phenomena which seem inconsistent with this explanation: in the first place if the current is reversed after flowing in one direction, traces of the former spectra linger for some time at the sides of the plates, and, secondly, if the difference is due to the greater decomposition at the negative side of the plate, how is it that in the case of the vapour of ethyl alcohol the hydrogen spectrum is not seen, at the commencement of the discharge, on the negative side of the plate? It only appears after the discharge has passed through for some time, when hydrogen has probably been set free by the decomposition of the vapour by the discharge. If the absence of the candle spectrum from the negative side

of the plate is due to the spark being so intense that the hydro-carbon which is supposed to be the origin of this spectrum cannot exist, then we ought to see the spectra of the substances which result from the decomposition of the hydro-carbon, *i.e.*, we ought to see the hydrogen spectrum at the negative electrode. The view which seems most in accordance with the results of observations on the discharge through these vapours is that the "candle spectrum" is the spectrum of carbon when the atom is charged with negative electricity, or of some compound of carbon in which its atom is negatively charged, while the "carbonic oxide" spectrum is the spectrum of carbon when the atom is charged with positive electricity, or of some compound in which the carbon atom is positively charged.

Discharge through an Elementary Gas.—It has long been known that when the discharge passes through some elementary gases, the spectra at the two electrodes are different. This was first shown to be the case for nitrogen, then Dr. Schuster showed that the same thing occurred with oxygen, and recently Mr. Crookes has shown that it is also true in the case of argon. I have observed a very striking change in the relative brilliancy of the red and green hydrogen lines at the two electrodes. When the tube with the plate across it was filled with hydrogen at a low pressure, then on the positive side of the plate the red line tends to be brighter than the green, while on the negative side the green line tends to be brighter than the red; in some tubes this was so marked that on the positive side of the plate the red line was bright, and the green invisible, while on the negative side of the plate the green line was bright, and the red invisible. The spectroscope I was using weakened the red rays much more than the green, so that I cannot be sure that the red rays were really altogether obliterated on the negative side of the plate; the above experiment is, however, sufficient to show that on the positive side of the plate the red rays are more easily excited than the green, while on the negative side the green line is more easily excited than the red. On the negative side of the plate we have an excess of positively charged hydrogen atoms, while on the positive side of the plate there is an excess of negatively charged hydrogen atoms, and I am inclined to attribute the difference in the spectra partly at any rate to the difference in properties between a positively and a negatively charged hydrogen atom. The reason I do not attribute it wholly to the difference in the potential gradient on the two sides of the plate is that the effect is not reversed immediately, but only gradually on reversing the coil, the former spectra clinging for some time to the sides of the plate.

Chlorine.—I have made a great many experiments to see if there is any difference between the spectra given by chlorine on the two

sides of the plate, but with negative results. Chlorine seems a gas in which we might expect to find this effect, for as Dr. Schuster, in his Report on Spectrum Analysis, says, the behaviour of its spectrum indicates that we have several spectra superposed. I have not, however, been able to effect a separation of its spectra, the differences I observed between the spectra on the two sides of the plate were irregular, and due, I think, to impurities producing effects like those observed when the discharge passes through a compound gas. However, as has been mentioned before, there is even in the case of gases where distinct evidence of separation can be obtained, a region of pressure within which the effects are irregular, and I ascribe my failure to observe separation in the case of chlorine to my having failed to get the relation between the intensity of the discharge and the pressure so adjusted as to get outside this irregular region. The cases, however, in which distinct differences between the spectra of a simple gas occur at the two electrodes, seem to indicate that the spectrum given by an element is influenced by the sign of the electrical charge carried by its atoms.

I have made some experiments to determine whether there was any separation produced in a mixture of equal volumes of hydrogen and chlorine kept in the dark, when a considerable difference of potential though not sufficient to produce discharge was maintained between the two electrodes. The parts of the tube adjacent to the two electrodes could be shut off from each other by a tap, and the amount of chlorine in the two sides was determined by absorbing it by caustic potash. The mixture was at atmospheric pressure, and the electrodes were maintained at a potential difference of about 1,200 volts by connecting them to a large battery of small storage cells. The potential difference between the terminals was maintained for about 16 hours on three separate occasions, but on analysing the vessels surrounding the two electrodes, the amount of chlorine in the vessel adjacent to the negative electrode did not differ from that in the vessel adjacent to the positive electrode by more than 1 per cent., and this could be accounted for by errors of experiments, as test experiments in which the mixture had not been exposed to the electric field gave differences comparable with these. We should conclude from the preceding experiments that the molecules of a gas are not acted on by any appreciable translational force tending to move them from one place to another, when they are near to a body charged with electricity. To test this point further, two large terminals were placed in bulbs which were connected by a horizontal capillary tube, in which a drop of sulphuric acid was placed; a difference in the pressure of the gas would cause the sulphuric acid to move, and the arrangement acts as a very delicate pressure gauge. The bulbs and tube were filled with

chlorine at atmospheric pressure. The terminals were then connected to the electrodes of a battery giving a potential difference of 1,200 volts, but not the slightest movement of the drop of acid could be detected.

I wish to acknowledge the help I have received in making the preceding experiment from my assistant, Mr. E. Everett.

X. "On the Evolution of the Vertebral Column of Amphibia and Amniota." By HANS GADOW, M.A., Ph.D., F.R.S.
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(Abstract.)

The key to the solution of the composition of the vertebral column is given by the metameric repetition of the four pairs of symmetrically arranged cartilaginous elements, the origin of which we have traced in Fishes, namely—

One pair of basidorsalia.

One pair of basiventralia (with its lateral outgrowths = ribs or pleurapophyses, and hæmal, ventral outgrowths = hæmal arches, chevrons, wedge-bones, hæmapophyses).

One pair of interdorsalia.

One pair of interventralia.

The first of these four pairs is always present and forms the neural arch. Of the other three pairs any one may be suppressed, sometimes even two in the same skleromere.

The vertebræ of the Amphibia and Amniota possess only arch-centra, because the chordal sheath takes no share in their formation.

According to the composition of these arco-genous centra or bodies we distinguish the following lines of evolution :—

I. Earliest primitive condition. All the four pairs of arcualia are present :—

1. Either as separate pieces, of which the interventralia are the smallest, *e.g.*, *Archegosaurus*, *Chelydosaurus*, *Larvæ of Urodela*.
2. Or the basidorsalia and basiventralia fuse together and form the middle of the vertebral body, while the interbasalia form neutral zones of intervertebral cartilage. Such PSEUDOCENTRA are those in the tail of *Urodela*.

II. The interventralia are reduced.

1. The other three pairs remain separate, and the interdorsalia tend to form the centrum. (NOTOCENTROUS